Outstanding effects of lignin addition in castor oil-based polyurethanes with elastomeric properties

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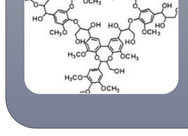
Introduction

The imperative to replace non-renewable materials by bio-based ones is propelling the search of renewable materials able to imitate the characteristics of well-known products. In the cushioning material field, the formulation of elastomers is mainly performed from non-renewable polymers. In the present study, the formulation of castor oil-based polyurethanes with elastomeric properties by reacting with hexamethylene diisocyanate (HDI) was aimed, characteristics which were significantly enhanced by the inclusion of lignin as a polyol/filler within the castor oil matrix. Different lignin contents as well as diverse lignin/HDI ratios were tested, which allowed to tune both the rheological and mechanical properties. Thus, the rheological response of the formulated systems ranged over four orders of magnitude, from soft materials with gel-like characteristics to very hard elastomers. Static tensile and compressive properties were also measured, whereas the dynamic properties of an optimal formulated system were also evaluated [1].

Experimental



Lignin modification

Indulin AT (MeadWestvaco, USA) was functionalized using different hexamethylene diisocyanate (HDI) w/w ratio (1/1-1/4), following a protocol described elsewhere [2].

Oleogel preparation

Functionalized lignin (FLs) were poured into castor oil at different concentrations (see Table 1) and stirred for 24 hours. Rheological and mechanical characterization was performed after curing.

Static mechanical characterization

Static tensile and compression tests were performed indistinctly in an AG-IS Universal Testing Machine (Shimadzu, Japan) and a 4204 Universal Tester (Instron, USA). Rates of 10 and 5 mm min^{-1} were applied for the tensile and compression tests.

Dynamic mechanical characterization

A TA.XT Plus Texture Analyser (Stable Micro Systems, UK) was used for dynamic mechanical characterization. Given loads (equivalent to 0.35–0.70 MPa) and test lengths (70 s–24 h) were applied at a constant compressive rate of 0.5 cycles·s^{-1}.

Rheological measurements

The rheological measurements were performed by using an ARES G2 (TA Instruments, UK). The small amplitude oscillatory and torsion tests (SAOS & SAOT, respectively) were performed by frequency sweeps from 0.03 to 100 rad·s^{-1}.

Results

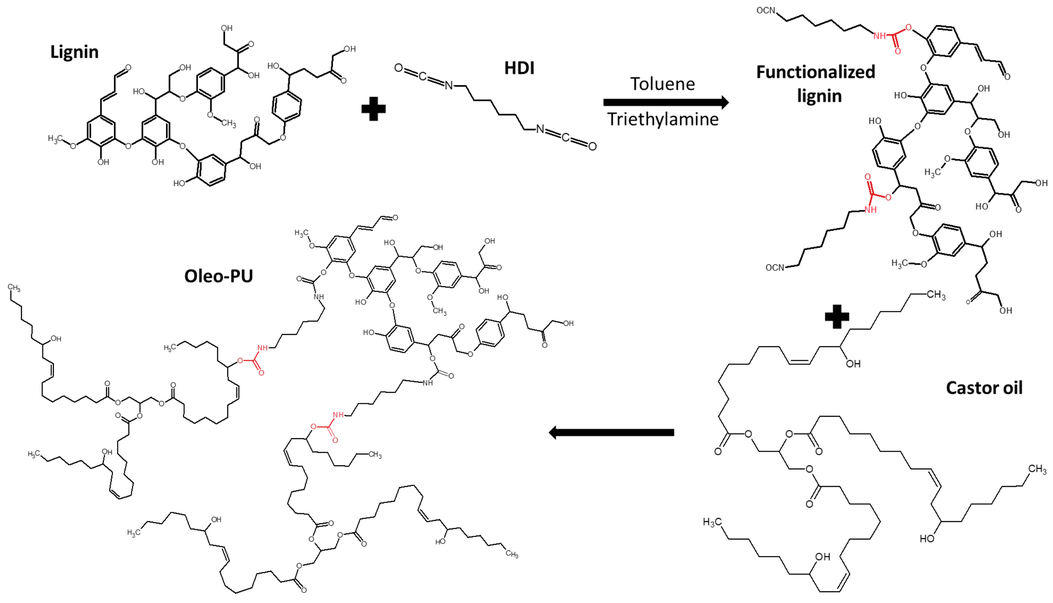


Figure 1. Reaction scheme for lignin functionalization and oleo-PU formation.

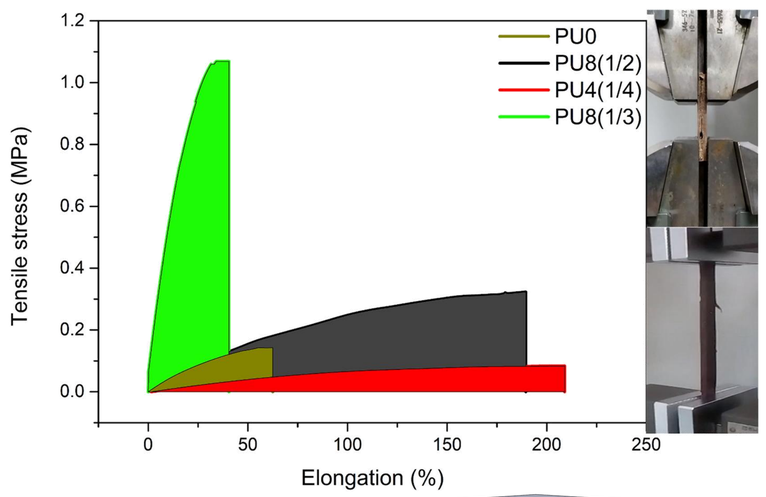


Figure 3. Tensile properties of developed elastomers.

Sample	Castor oil (wt%)	Lignin (wt%)	HDI (wt%)
PU0	83.33	0	16.67
PU8(1/2)	75.00	8.33	16.67
PU4(1/4)	79.16	4.16	16.67
PU17(1/1)	66.66	16.67	16.67
PU8(1/1)	83.34	8.33	8.33
PU8(1/3)	66.66	8.33	25.00
		Cellulose (wt%)	
CEL-PU	75.00	8.33	16.67
		Silica nanoparticles (wt%)	
SIL-PU	75.00	8.33	16.67

Table 1. Composition of the oleo-PUs

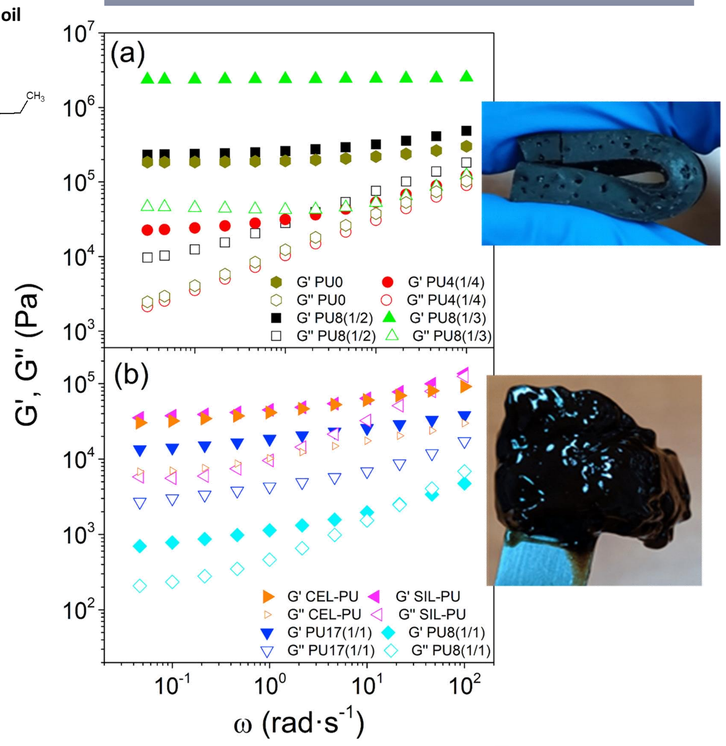
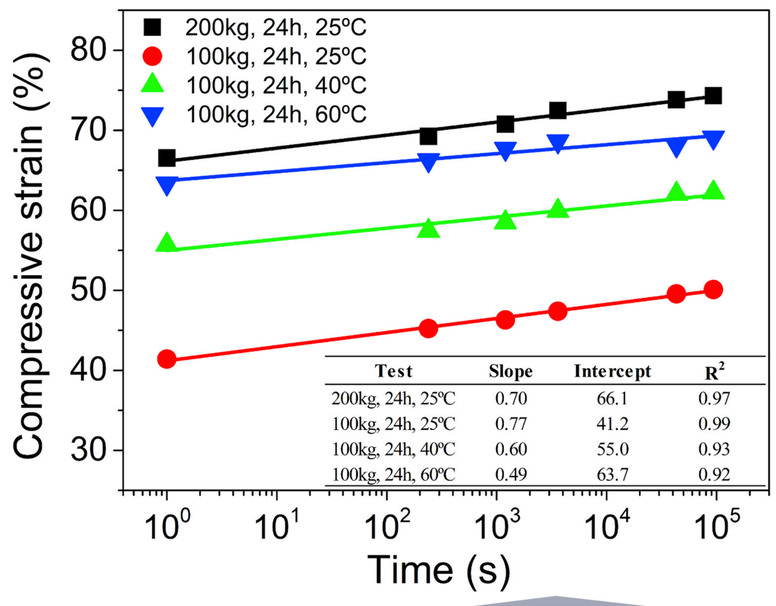


Figure 2. Viscoelastic responses of lignin-based elastomers and gel-like systems (top and bottom, respectively).



Test	Slope	Intercept	R^2
200kg, 24h, 25ºC	0.70	66.1	0.97
100kg, 24h, 25ºC	0.77	41.2	0.99
100kg, 24h, 40ºC	0.60	55.0	0.93
100kg, 24h, 60ºC	0.49	63.7	0.92

Figure 4. Compressive strain evolution with time under different loads and temperatures for PU8(1/2)

Conclusions

- Adjusting lignin or HDI concentration allows tailoring the rheological properties, obtaining from very soft to strong materials.
- The tensile strain at break of lignin loaded polyurethanes was triplicated by replacing a small fraction of castor oil with lignin (4.17 wt.%).
- At higher lignin content, 8.33 wt.%, the PU maintained the elongation but presented 17- and 7-fold increases in the Young modulus and the stress at break, respectively.
- According to the compression tests, lignin addition (4.17 wt.%) withstood > 88% strain without failure, an improvement of >38% compared to PU0, and exhibited a 4-times higher stress at break (3 MPa).
- A superior lignin addition (8.33 wt.%), extended the outstanding properties, with a strain at failure of 93%, while the stress at break was 88-fold higher compared to the reference system.
- Outstanding short- and long-term dynamic compression properties were shown, such as time-independent energy absorption evolution, outstanding resilience in long term high-load fatigue tests, and a fast release of the absorbed energy during the compression.

References

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